

File 9
September 15
UNITED STATES

PROJECT _____

CENTRAL FILE NUMBER
43-6-151

Those Eligible
To Read The
Attached

Copy # 8:

Copy # 8:
S. H. Pratt

OK
~~Ben~~
 Vaughan
 Clinton L. Fife

Date **June 21, 1943**

Subject Phosphate Process Waste Disposal *for* 13.

By **F. S. Chambers**

To L. Squires

Before reading this document, sign and date below

| Name | Date |
|-----------------------|-----------------|
| Pratt-reen | 6/22 |
| Kay | 6/22 |
| ✓ B. Vaughan | 6/22 |
| W. A. Rosenberg | 6/23 |

[illegible]

~~This document has been approved for release to the public by:~~

David R. Harriman 5/26/95
Technical Information Officer Date
ORNL Site

#2017

SEP 18 1963

U. S. Atomic Energy Commission

Chief, Publication Branch

- 5 10
- 1 - L. Squires
 - 2 - File 1
 - Greenwalt
 - Graves
 - Williams
 - 3 - File 2
 - Graves
 - Technical
 - 4 - J. B. Miles
 - 5 - R. M. Evans
 - 6 - R. M. Evans
 - 7 - S. W. Pratt
 - 8 - S. W. Pratt
 - 9 - F. S. Chambers
 - 10 - Chronological

June 21, 1943

MEMORANDUM

SECRET

TO: L. SQUIRES

FROM: F. S. CHAMBERS

CONFIDENTIAL

PHOSPHATE PROCESS WASTE DISPOSAL

As you know the desirability of transporting waste solutions containing precipitated solids between the canyon and the waste disposal area has been questioned because of the possibility of these solids causing stoppages in lines which will be inaccessible. While a partial solution to this problem would be effected by neutralizing in the disposal area, this would be extremely undesirable process-wise. Consequently a re-evaluation of the methods of neutralizing waste solutions and slurries was made, with the goal that all the neutralized liquors should be either clear solutions or slurries containing less than 2% by weight of flocculent solids. A preliminary solution to this problem has been obtained and a flowsheet drawn up on that basis.

The waste metal solution from the extraction step appeared to be the one most likely to cause trouble. While the waste from the fluoride process when neutralized to a pH of 7 is only a thin slurry which might conceivably be handled without undue difficulty, that from the phosphate process could not be handled since all the solids are precipitated on neutralization. It was suggested that the addition of fluoride ion to this solution might result in the formation of a fluoride complex which is believed to be responsible for preventing precipitation during neutralization of the wet B waste solution. It was also suggested that the wet B process by-product precipitation procedure be employed for introducing fluoride ion, since by this technique the waste metal solution would be substantially decontaminated and the more active by-products would be isolated. This, of course, would greatly facilitate the ultimate recovery of either of these materials.

During the week of June 7, samples of the waste metal from the semiworks phosphate run, C 25, were treated in the laboratory by making barium sulfate, zirconium phosphate, and lanthanum fluoride precipitates. It was found, however, that this procedure resulted in only a minor improvement in the neutralization characteristics of phosphate wastes. While solids began to precipitate from untreated waste at acidities higher than $\text{pH} = 0$ and a thick gel was formed at $\text{pH} = 0.5$ (which broke up on further neutralization), and precipitation was complete at $\text{pH} = 6$, the treated waste started to precipitate between $\text{pH} 1$ and 2 . Precipitation was 75% complete at $\text{pH} = 4$, and 90% complete at $\text{pH} = 6$.

It was found, however, that if the phosphate metal wastes were neutralized with an excess of sodium carbonate, a soluble uranium carbonate complex was formed. While this neutralization foamed badly when the alkali was added to the metal solution, if the reverse procedure was used the foaming was very slight and no intermediate precipitate was formed. Approximately 300 gms. of sodium carbonate were required per liter of waste in the several laboratory-scale neutralizations that were made, this being equivalent to 3 tons of soda ash per ton of metal. It was also observed that the complex could not be formed if either fluoride or chloride ions were present, and is destroyed if sodium hydroxide is added to the solution. While this method obviated the necessity of decontaminating the metal waste to make it satisfactory for handling, the preliminary flowsheet has been drawn up to include the removal of barium sulfate and zirconium phosphate precipitates, along with the lanthanum and cerium carbonates which are precipitated during neutralization, since it is probable that this treatment will remove about 90% of the activity from the metal and will provide the extra waste tanks and the extra canyon equipment that would be required if the fluoride process were to be operated.

The most troublesome of the remaining wastes appear to be the granular bismuth phosphate decontamination by-product precipitates. It was found, however, that when this precipitate was dissolved in nitric acid and reprecipitated by neutralization with either sodium hydroxide or sodium carbonate, it comes down as a flocculent, slow settling precipitate. With the present cake dissolving ratio, this slurry is less than 2% solids. The use of lower nitric ratios will probably mean that water will have to be added to reduce the concentration of solids to a satisfactory level.

The neutralization of coating solutions was not studied, since it is known that an excess of sodium hydroxide will convert the aluminum nitrate to soluble sodium aluminate. This step will, of course, have to be studied to determine the exact quantity of alkali required.

~~CONFIDENTIAL~~

It does not appear that there will be any problem in neutralizing the decontamination mother liquors, since these will be clear solutions except for traces of iron and chromium hydroxide. If, however, any major changes are considered in either the decontamination, oxidation, or reduction procedures, the effect of these changes on the neutralization characteristics of the wastes will have to be determined.

The preliminary flowsheet has been made up to provide for dividing the wastes 3 ways:

1. Waste metal solution which can be stored in concrete tanks. This will amount to 4,250 gallons per day and contain about 10% of the radioactivity.
2. Steel tanks for the storage of metal waste decontamination and the first decontamination by-product precipitates. These will handle 730 gallons of slurry containing less than 2% solids per day. Approximately 90% of the activity should be contained in these wastes.
3. Storage for low activity wastes. These tanks will contain the coating solution, the decontamination mother liquors, and the second and third decontamination by-product precipitates. While the volume of these liquors will be 3,210 gallons per day, the activity should be low enough to permit the use of partially buried tanks or even open ponds.

The following procedure has been worked out for W wastes. The metal waste neutralization cells will be located in the canyon between the extraction and decontamination cells. The equipment consists of a precipitator, a centrifuge, a filtrate catch tank, and a cake receiving tank. In operation, the waste metal solution will be received in the precipitator. The zirconium and barium are added, the slurry held for an hour at room temperature to permit precipitate formation and then centrifuged. The cake is skimmed and given two water washes and held in the bowl. It is believed that the washing is necessary to prevent foaming during the second filtration of the cycle and to remove acidity to reduce corrosion in the event that this precipitate heats up materially during the retention period. The filtrate in the catch tank is then jetted back to the precipitator which has been previously charged with the required quantity of 30% soda ash solution. After neutralization, the solution is again centrifuged to remove the precipitated lanthanum and cerium carbonates and is then jetted to the proper storage tank. It is planned, at present, to remove the by-product cake from the centrifuge bowl by slurrying in water. This water will be introduced through fish tail jets so that cake adhering to the walls can be washed down.

It seems probable that the intermediate filtration step outlined above will prove to be unnecessary, although the effect of prolonged contact with alkali on zirconium phosphate will have to be determined before this can be done.

~~SECRET~~

It has been planned to also handle the by-product cake from the first decontamination in this cell. This will be jetted as a solution in nitric acid from the decontamination cell and will be neutralized either with 10% excess caustic or soda ash in the centrifuge cake receiving tank and will be sent to the by-product storage tanks.

The decontamination wastes would be handled in a cell located between the first and second decontamination cells containing 1 or 2 agitated neutralizing vessels. It is planned to neutralize the decontamination mother liquors, the later by-product precipitate solutions, and the coating solution in these tanks, using a 10% excess of caustic in each case. To simplify piping to this cell, it will probably be desirable to equip one of the dissolver cells with a small tank which will receive the coating solution and washing from the 3 dissolvers and from which this liquor can be transferred to the neutralizer. The neutral solutions and slurries from this neutralizer will, of course, be jetted to the decontamination waste storages.

A 10% excess of alkali was specified for these neutralizations so that pH control would be unnecessary. The presence of an excess of free alkali in these tanks would permit the occasional delivery of an unneutralized charge whenever it appeared that solids were accumulating in the lines.

There are a number of factors in this setup which will require further investigation at the Metallurgical Laboratory:

1. While it is estimated that 90% or more of the activity can be removed from the metal waste solution by decontaminating, this step should be investigated on both the laboratory and semiworks scales. Special emphasis should, of course, be put on the effectiveness of the proposed lanthanum carbonate and cerium carbonate precipitates. In addition, the possibility of eliminating the intermediate filtration shown on the flowsheet should be investigated.
2. The distribution ^{of} activity between the various wastes should be determined so that the proper cooling facilities for the by-product waste tanks can be designed and the shielding necessary for the decontamination wastes can be specified.
3. The quantity of alkali required to convert the aluminum nitrate in the coating solution to sodium aluminate should be determined experimentally. In addition, it would be desirable to determine whether this solution can be neutralized with soda ash without precipitating aluminum, since conditions at X make it desirable to use 1 neutralizing agent for all steps.

~~SECRET~~

4. An extensive study of centrifuging the various precipitates obtained in the metal decontamination step is in order, since zirconium phosphate is already known to be a bad actor and since the lanthanum and cerium carbonates are also extremely flocculent. In the flowsheet, the centrifuging rate was set at half of that used for lanthanum fluoride because of the possible bad characteristics of these precipitates. The effect of eliminating the intermediate filtration should, of course, be studied.

~~SECRET~~